Atmos. Chem. Phys. Discuss., 13, 8213–8231, 2013
www.atmos-chem-phys-discuss.net/13/8213/2013/
doi:10.5194/acpd-13-8213-2013

Atmospheric Chemistry and Physics Discussions

^{222}Rn calibrated mercury fluxes from terrestrial surface of southern Africa derived from observations at Cape Point, South Africa

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Received: 18 February 2013 – Accepted: 15 March 2013 – Published: 26 March 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Gaseous elemental mercury (GEM) and ^{222}Rn, a radioactive gas of primarily terrestrial origin with a half-life of 3.8 days, have been measured simultaneously at Cape Point, South Africa, since March 2007. Between March 2007 and December 2011 altogether 191 events with high ^{222}Rn concentrations were identified. GEM correlated with ^{222}Rn in 94 of the events and was constant during almost all the remaining events without significant correlation. The average GEM/^{222}Rn emission ratio of all events including the non-significant ones was -0.0001 ± 0.0030 pg mBq^{-1}, with 0.0030 pg mBq^{-1} being the standard error of the average. With an emission rate of 1.1 ^{222}Rn atoms cm^{-2} s^{-1} and a correction for the transport duration, this emission ratio corresponds to a radon calibrated flux of about -0.01 ng GEM m^{-2} h^{-1} with a standard error of ± 0.34 ng GEM m^{-2} h^{-1} (n = 191). With wet deposition, which is not included in this estimate, the terrestrial surface of southern Africa seems to be a net mercury sink of about -1.01 ng m^{-2} h^{-1}.

1 Introduction

Mercury poses a serious environmental problem, because of its transformation to methyl mercury in the aquatic environment which is a potent toxin to humans and animals (Mergler et al., 2007; Scheuhammer et al., 2007). Of primary concern are thus the emissions of mercury into the atmosphere, which due to long atmospheric residence time of elemental mercury (Lindberg et al., 2007) can be distributed all over the world. According to the current emission inventories and models, anthropogenic emissions represent with 2880 t yr^{-1} the largest mercury source followed by 2680 t yr^{-1} from the oceans and 1850 t yr^{-1} from the terrestrial surfaces (Mason, 2009; Pirrone et al., 2010). Whereas anthropogenic emissions are believed to be known with an uncertainty of ±30 %, the emissions from oceans and terrestrial surfaces are considered to be more uncertain by about ±50 % (Lin et al., 2006; Lindberg et al., 2007).

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The uncertainties related to emissions from terrestrial surfaces originate mostly from the poor knowledge of the emission mechanisms, the worldwide up-scaling of a small number of field measurements made in a few geographic regions, and the measurement challenges (Lindberg et al., 2007; Gustin et al., 2008; Mason, 2009; Smith-Downey et al., 2010). Mercury emission from terrestrial surfaces is dependent on meteorological conditions, type of soil and vegetation, and historical atmospheric deposition (Zhang and Lindberg, 1999; Gustin et al., 2000, 2008; Gustin, 2003; Song and Van Heyst, 2005; Bash, 2010; Smith-Downey et al., 2010). The influence of these parameters has been studied in the laboratory and in the field but the underlying mechanisms are still not well understood (Mason, 2009). The flux can be bi-directional depending on the mercury concentration in ambient air: deposition at higher concentrations and emission at lower concentrations with a cross-over point termed "compensation point" (e.g. Hanson et al., 1995; Lindberg et al., 1998; Zhang et al., 2009). An intercomparison of field flux measurement techniques revealed substantial disparities between the chamber and the micrometeorological methods (Gustin and Lindberg, 2000). In addition to all these problems, field flux measurements have so far been carried out almost exclusively in temperate regions of North America and Europe. Their scaling up to other regions in the Northern and Southern Hemisphere is thus necessarily fraught with large additional uncertainties.

^{222}Rn is a radioactive gas of predominantly terrestrial origin with a half-time of 3.8 days. Its emission rate from soil is relatively evenly distributed (Zhang et al., 2011 and references therein) making ^{222}Rn a good tracer for studies of emissions from terrestrial surfaces (Zahorowski et al., 2004). According to Jacob et al. (1997) the assumption of a uniform ^{222}Rn emission rate of 1 atom cm^{-2} s^{-1} is accurate to roughly 25 % globally, or a factor of 2 regionally. ^{222}Rn has been successfully used to derive regional emissions of CO_2, CH_4, and N_2O (e.g. Gaudry et al., 1990; Wilson et al., 1997; Zahorowski et al., 2004; Hirsch, 2007). To the best of our knowledge its only application to mercury flux estimations has been reported by Obrist et al. (2006). They found good agreement between fluxes estimated from the accumulation of Hg and ^{222}Rn in the stable noc-

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turnal boundary layer and those measured by a micrometeorological technique of the modified Bowen ratio. The major advantage of the Hg/^{222}Rn method is its capability to estimate regional fluxes and by this to avoid shortcomings related to up-scaling of point measurements in the field (Wilson, et al., 1997; Obrist et al., 2006). In this paper we use concurrent measurements of gaseous elemental mercury and ^{222}Rn at Cape Point, South Africa, to derive the regional mercury flux from southern Africa.

2 Experimental

The Cape Point station (34°21′ S, 18°29′ E) is part of the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) network. Cape Point is about 60 km south of Cape Town, and located on top of a coastal cliff 230 m a.s.l. at the southernmost tip of the Cape Peninsula. The site is located in a nature reserve and experiences moderate temperatures, dry summers with occasional biomass burning episodes in the surrounding area and increased precipitation during austral winter. The dominant wind direction is from the south-eastern sector which is representative of clean maritime air from the Southern Ocean (Brunke et al., 2004). The site is occasionally also subjected to air from the northern to north-eastern sector (mainly during austral winter), which is influenced by anthropogenic emissions from the greater Cape Town area and/or by other continental sources (both local and regional).

Within the framework of the WMO-GAW program, continuous trace gas measurements of CO_2, CH_4, CO and O_3 have been made at Cape Point for more than 30 yr now (Scheel et al., 1990). The ^{222}Rn measuring program started in 1999 and serves mostly to classify air masses into maritime, continental or mixed (Brunke et al., 2004). Gaseous mercury concentrations have been measured discontinuously (about 200 samples per year) since September 1995 (Slemr et al., 2008) and continuously with a resolution of 15 min since March 2007 (Brunke et al., 2010). Only the high resolution data until the end of 2011 were used in this work.

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Continuous measurements of gaseous mercury are made using a Tekran 2537A vapour-phase mercury analyzer (Tekran Inc., Toronto, Canada). It is capable of measuring low level mercury concentrations typically observed at background locations (Ebinghaus et al., 1999; Munthe et al., 2001). The analyzer is operated in an air-conditioned laboratory and run with a sampling air flow rate of 1 L min^{-1} at 15 min sampling intervals. The span of the analyzer is checked by an internal permeation source once every 25 h. The air sample intake was attached to a 30-m high aluminium sampling mast at a height of approximately 5 m above the rocky surface and about 235 m a.s.l. A Teflon filter (pore size 0.2 µm; ID = 45 mm) upstream of the instrument protects the analyzer against contamination by particulate matter. The filter was replaced once every two weeks. The TGM detection limit with a 15 min sampling interval is about 0.05 ng m^{-3}. The 15-min TGM data have been converted to 30-min averages so that comparisons with other trace gas and meteorological data being measured simultaneously at Cape Point could be made. Under the prevailing atmospheric conditions at Cape Point (higher temperature and air humidity, in addition to hygroscopic sea salt aerosols) we assume that reactive gaseous mercury (RGM) will be adsorbed by the inlet tubing and the aerosol filter and that the measured atmospheric mercury concentration thus represents exclusively Gaseous Elemental Mercury (GEM) (Brunke et al., 2010).

Since 1999 a ^{222}Rn detector designed by the Australian Nuclear Scientific & Technology Organisation (ANSTO) and manufactured by AGH Industries (Riverwood, Australia), had been installed at Cape Point. The so-called two-filter instrument is described in detail by Whittlestone and Zahorowski (1998) and Brunke et al. (2002). Briefly, radon and thoron decay products are removed from the air by the first filter. Decay products newly formed under controlled conditions in the instrument delay tank are then retained by a second filter. Their alpha radiation is then determined by a zinc sulfide scintillator. The detection limit of the instrument at Cape Point is quoted to be 33 mBq m^{-3} (Brunke et al., 2002).

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Hg vs. ^{222}Rn was correlated using orthonormal regression (Cantrell, 2008) which takes the uncertainties of both correlated parameters into account. Factors affecting the sensitivity and accuracy of the Cape Point ^{222}Rn detector have been discussed by Brunke et al. (2002) and by references therein. For the correlations here, the GEM and ^{222}Rn uncertainties were set to 0.05 ng m^{-3} and 50 mBq m^{-3}, respectively.

The regions of origin for the pollution events were interpreted using ten-day isentropic back trajectories from NOAA ESRL (http://www.esrl.noaa.gov/gmd) and seven-day back trajectories calculated by NILU using the FLEXTRA model (http://nadir.nilu.no/trajectories/files/png).

3 Results and discussion

Altogether 191 events with ^{222}Rn concentrations above 1000 mBq m^{-3}, which lasted usually for more than a day or more, have been identified between March 2007 and December 2011. Their seasonal occurrence frequency is shown in Fig. 1. Most of them occur in the months March–September, in agreement with the climatology of Cape Point (Brunke et al., 2004). The events can extend up to 7 days, but most of them last 2–4 days. Their duration is thus substantially longer than that of the depletion events or the typical pollution plumes observed at Cape Point which generally last only several hours (Brunke et al., 2010, 2012). This difference allows us to discriminate against the depletion events, the anthropogenic emissions and emission from biomass burning. 56 events with enhanced ^{222}Rn concentrations coincided with such depletion and pollution events. For the subsequent analysis of the relationship between Hg and ^{222}Rn from terrestrial emissions, these short depletion and pollution events were eliminated.

Figure 2 shows the frequency distribution of the GEM/^{222}Rn slopes from the correlations. In 94 events the correlations were significant at least at the 95 % significance level. The insignificant correlations for the remaining events may either imply that there is no relation whatsoever or that the GEM concentration remains constant during the ^{222}Rn event. Figure 2 shows that the latter is the case: the largest difference

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between the frequency of all and significant GEM/^{222}Rn slopes is in the bin with the central value of 0 pg mBq^{-1}, followed by the bins with the central values −0.02, +0.02, and +0.04 pg mBq^{-1}. In the remaining bins almost all correlations are significant. Thus the 97 events with insignificant GEM vs. ^{222}Rn correlations and a slope close to zero still provide meaningful information about the net GEM flux between the surface and the atmosphere and we have included them in subsequent analyses. The average GEM/^{222}Rn slope of all 191 events is -0.0001 ± 0.0421 pg mBq^{-1} which is statistically indistinguishable from the average of -0.0057 ± 0.0492 pg mBq^{-1} for 94 events with significant correlations. Both averages cannot be statistically distinguished from zero flux.

Figure 3 shows the intercepts and the slopes of all GEM vs. ^{222}Rn correlations in the upper and lower panel, respectively. The intercepts represent the background mercury concentrations at Cape Point. They vary between 0.69 and 1.15 ng m^{-3} and average 0.92 ± 0.10 ng m^{-3} for all correlations and 0.93 ± 0.10 ng m^{-3} for the significant ones. The intercepts do not show any apparent seasonal variation. The slopes vary between −0.105 and +0.178 pg mBq^{-1} and they also do not show any pronounced dependency on season. This suggests that temperature is not the major parameter influencing the terrestrial GEM fluxes in southern Africa. A plot of the slopes against the intercepts (not shown) also does not reveal any dependence of the flux on ambient GEM concentration.

Two backward trajectories for the ^{222}Rn events are shown in Fig. 4: one for 12:00 UTC of 24 February 2009 (upper panel), and for 06:00 UTC of 2 April 2008 (lower panel). Both look similar and are typical for most of the ^{222}Rn events presented here. They encompass usually South Africa and the neighbouring countries of Namibia, Botswana, Zimbabwe, and Mozambique. The GEM/^{222}Rn flux ratio was $+0.089 \pm 0.019$ pg mBq^{-1} for the event on 3 May 2008 (4th highest of all events with significant correlations). However, the event on 2 April 2008 (the lowest of all events with significant correlations) had a flux ratio of merely -0.030 ± 0.007 pg mBq^{-1}. This

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and the trajectory analysis of other events could not reveal any systematic dependence of the terrestrial flux ratios on backward trajectories.

Precipitation is known to stimulate the emission of mercury from soils, especially in arid regions (e.g. Song and Van Heyst, 2005; Cobbett et al., 2007; Xin et al., 2007). Therefore, the occurrence of precipitation was investigated for 7 of the events with the highest emission and 5 events associated with the highest deposition. The events with the highest emission were more frequently connected to intermediate rain over southern Africa (4 events) than those with highest deposition (1 event), suggesting indeed some degree of stimulation of mercury emissions by precipitation.

The terrestrial surface of southern Africa is presumed to emit about 1.1 ^{222}Rn atoms cm^{-2} s^{-1} corresponding to 23.1 mBq m^{-2} s^{-1} (Griffiths et al., 2010; Zhang et al., 2011). With this emission rate the radon calibrated GEM flux of southern Africa varied between −8.7 and +14.8 ng m^{-2} h^{-1}. The average flux of all events and those with significant correlations only was -0.01 ± 3.50 and -0.47 ± 4.09 ng m^{-2} h^{-1}, respectively. For comparison with other measurements and models the standard error of the mean fluxes of 0.25 and 0.42 ng m^{-2} h^{-1} for all events and events with significant correlation, respectively, may be more informative. ^{222}Rn decay has not been considered in these estimates. Assuming an average transport time of 2 days, the absolute flux values would increase by about 36 % if ^{222}Rn decay were considered to -0.01 ± 4.76 ng m^{-2} h^{-1} (±0.34 ng m^{-2} h^{-1} standard error of the average) for all events and -0.64 ± 5.56 ng m^{-2} h^{-1} (±0.57 ng m^{-2} h^{-1} standard error of the average) for the ones with significant correlation. To the best of our knowledge we are not aware of any long-term measurements of mercury species over southern Africa. Reactive gaseous mercury concentration in the marine boundary layer around southern Africa is smaller than 7 pg m^{-3} (Soerensen et al., 2010) representing less than 1 % of the GEM concentration. Assuming the concentration of particulate mercury being in the same range (Slemr et al., 1985), the fluxes derived here represent the dry total mercury flux.

The terrestrial surface of southern Africa might be quite unique due to its arid characteristics. But the essentially net zero flux derived here compares quite well with low

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fluxes of $0.4 \pm 0.5\,ng\,m^{-2}\,h^{-1}$ measured over a period of 1 yr on the forest floor in Standing Stone State Forest in Tennesse (Kuiken et al., 2008a), and with $0.2 \pm 0.9\,ng\,m^{-2}\,h^{-1}$, measured at six forested sites in different states of eastern USA (Kuiken et al., 2008b). Average net emissions of 1.71 (estimate from 1.14 to 4.55) and 1.60 (estimate from 0.86 to 3.20) $ng\,m^{-2}\,h^{-1}$ can be derived from Table 7.5 of the compilation by Mason (2009) for deserts/metalliferrous zones and savannah regions, respectively, in tropical/subtropical regions. Taken as fixed values, these emissions are statistically significantly larger (> 99 %) than our average radon calibrated flux rates. A soil model by Smith-Downey et al. (2010) predicts even larger gross emissions – up to $4.6\,ng\,m^{-2}\,h^{-1}$ – from southern African soils. However, these emissions are compensated by wet and dry deposition of the same magnitude resulting in a much smaller net flux which is comparable to our measurement.

The radon calibrated fluxes derived by us do not include mercury wet deposition. Precipitation measurements at Cape Point from June 2007 to December 2009 yield an average wet deposition of $-1.01\,ng\,m^{-2}\,h^{-1}$ (Gichuki and Mason, 2013). The GEOS model by Selin et al. (2008) predicts a wet deposition flux of about −0.34 to $-0.11\,ng\,m^{-2}\,h^{-1}$ for pre-industrial times in southern Africa and an enrichment factor of ∼ 4 due to anthropogenic activities yielding a current deposition of about −1.37 to $-0.46\,ng\,m^{-2}\,h^{-1}$. An improved GEOS model by Soerensen et al. (2010) predicts a wet deposition flux of $-1.10\,ng\,m^{-2}\,h^{-1}$ for Cape Point. Thus the wet deposition predicted by both models agrees well with the measurements of Gichuki and Mason (2013). Assuming an average wet deposition flux of $-1.01\,ng\,m^{-2}\,h^{-1}$, the net deposition over southern Africa would be $-1.01\,ng\,m^{-2}\,h^{-1}$ with a standard error of $0.34\,ng\,m^{-2}\,h^{-1}$ when all events and only the standard error of the radon calibrated flux are taken into account. The terrestrial surface of southern Africa thus seems to be a net sink for atmospheric mercury. The GEOS model by Selin et al. (2008) predicts soils to be a net mercury sink of some $-0.61\,ng\,m^{-2}\,h^{-1}$, if re-emission by biomass burning is excluded and the flux to all terrestrial surfaces is considered to be the same. The exclusion of biomass burning is justified, since we excluded the short pollution events from our radon cali-

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brated fluxes. The model predicted net deposition rate is thus somewhat smaller but in reasonable agreement with our radon calibrated fluxes, considering their standard error and the uncertainty of the wet deposition. More data on wet deposition in southern Africa would further constrain the uncertainty of the net mercury deposition in this area.

4 Conclusions

Radon calibrated fluxes of mercury over terrestrial surface of southern Africa were derived from concurrent measurements of GEM and ^{222}Rn at Cape Point between March 2007 and December 2009. The average dry mercury flux over this period was with $-0.01 \pm 0.34\,\mathrm{ng\,m^{-2}\,h^{-1}}$ (standard error with n = 191, after correction for ^{222}Rn decay) not statistically distinguishable from zero. No apparent seasonal flux variation was observed and the fluxes were not dependent on the ambient mercury concentration. However, there is some tenuous evidence suggesting that precipitation can stimulate mercury emissions. The fluxes derived here tend to be smaller than fluxes measured at mid-latitudes of the Northern Hemisphere and than the emissions predicted by the models. By including wet mercury deposition ($-1.01\,\mathrm{ng\,m^{-2}\,h^{-1}}$) the terrestrial surface of southern Africa thus represents a significant net sink for atmospheric mercury of $-1.01\,\mathrm{ng\,m^{-2}\,h^{-1}}$. This net sink is somewhat larger but in reasonable agreement with the net mercury flux of $-0.61\,\mathrm{ng\,m^{-2}\,h^{-1}}$ predicted by the GEOS model (Selin et al., 2008).

We believe, however, that the agreement of the fluxes determined here with those predicted by models should be viewed with caution. The uncertainty of wet deposition fluxes over southern Africa are still too large due to the lack of measurements. The extrapolation of our results to other areas is also not possible. Mercury emissions from soils are dependent on soil humidity (Song and Van Heyst, 2005) and can be expected to be smaller in arid southern Africa than elsewhere. Being located in the Southern Hemisphere, southern Africa has also received less historical mercury deposition than

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comparable regions in the Northern Hemisphere, probably leading to smaller emissions or even a net deposition of mercury imported from the Northern Hemisphere. Consequently, determination of radon calibrated mercury fluxes in other regions would be highly desirable.

Acknowledgements. We are grateful towards D. van der Spuy for having assisted in data preparation. By the same token the assistance rendered by B. Parker and T. Mkololo in maintaining the Tekran 2537A analyser at Cape Point in good working order has been greatly appreciated. Furthermore, we are also grateful to NOAA for having made available isentropic 10-day backward trajectories and to NILU for 7-day backward trajectories.

The service charges for this open access publication
have been covered by the Max Planck Society.

References

Bash, J. O.: Description and initial simulation of a dynamic bidirectional air-surface exchange model for mercury in Community Multiscale Air Quality (CMAQ) model, J. Geophys. Res., 115, D006305, doi:10.1029/2009JD012834, 2010.

Brunke, E.-G., Labuschagne, C., Parker, B., van der Spuy, D., and Whittlestone, S.: Cape Point GAW station ^{222}Rn detector: factors affecting sensitivity and accuracy, Atmos. Environ., 36, 2257–2262, 2002.

Brunke, E.-G., Labuschagne, C., Parker, B., Scheel, H. E., and Whittlestone, S.: Baseline air mass selection at Cape Point, South Africa: application of ^{222}Rn and other filter criteria to CO_2, Atmos. Environ., 38, 5693–5702, 2004.

Brunke, E.-G., Labuschagne, C., Ebinghaus, R., Kock, H. H., and Slemr, F.: Gaseous elemental mercury depletion events observed at Cape Point during 2007–2008, Atmos. Chem. Phys., 10, 1121–1131, doi:10.5194/acp-10-1121-2010, 2010.

Brunke, E.-G., Ebinghaus, R., Kock, H. H., Labuschagne, C., and Slemr, F.: Emissions of mercury in southern Africa derived from long-term observations at Cape Point, South Africa, Atmos. Chem. Phys., 12, 7465–7474, doi:10.5194/acp-12-7465-2012, 2012.

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13, 8213–8231, 2013

Cantrell, C. A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmos. Chem. Phys., 8, 5477–5487, doi:10.5194/acp-8-5477-2008, 2008.

Cobbett, F. D. and Van Heyst, B. J.: Measurement of GEM fluxes and atmospheric mercury concentrations (GEM, RGM and Hg^P) from an agricultural field amended with biosolids in southern Ontario, Canada (October 2004–November 2004), Atmos. Environ., 41, 2270–2282, 2007.

Ebinghaus, R., Jennings, S. G., Schroeder, W. H., Berg, T., Donaghy, T., Guentzel, J., Kenny, C., Kock, H. H., Kvietkus, K., Landing, W., Mühleck, T., Munthe, J., Prestbo, E. M., Schneeberger, D., Slemr, F., Sommar, J., Urba, A., Wallschläger, D., and Xiao, Z.: International field intercomparison measurements of atmospheric mercury species at Mace Head, Ireland, Atmos. Environ., 33, 3063–3073, 1999.

Gaudry, A., Polian, G., Ardouin, B., and Lambert, G.: Radon-calibrated emissions of CO_2 from South Africa, Tellus B, 42, 9–19, 1990.

Gichuki, S. W. and Mason, R. P.: Mercury and metals in South African precipitation, Atmos. Environ., in review, 2013.

Griffiths, A. D., Zahorowski, W., Element, A., and Werczynski, S.: A map of radon flux at the Australian land surface, Atmos. Chem. Phys., 10, 8969–8982, doi:10.5194/acp-10-8969-2010, 2010.

Gustin, M. S.: Are mercury emissions from geologic sources significant? A status report, Sci. Total Environ., 304, 153–167, 2003.

Gustin, M. S. and Lindberg, S. E.: Assessing the contribution of natural sources to the global mercury cycle: the importance of intercomparing dynamic flux measurements, Fresenius J. Anal. Chem., 366, 417–422, 2000.

Gustin, M. S., Lindberg, S. E., Austin, K., Coolbaugh, M., Vette, A., and Zhang, H.: Assessing the contribution of natural sources to regional atmospheric mercury budgets, Sci. Total Environ., 259, 61–71, 2000.

Gustin, M. S., Lindberg, S. E., and Weisberg, P. J.: An update on the natural sources and sinks of atmospheric mercury, Appl. Geochem., 23, 482–493, 2008.

Hanson, P. J., Lindberg, S. E., Tabberer, T. A., Owens, J. G., and Kim, K.-H.: Foliar exchange of mercury vapor: evidence for a compensation point, Water Air Soil Pollut., 80, 373–382, 1995.

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13, 8213–8231, 2013

Hirsch, A. I.: On using radon-222 and CO_2 to calculate regional-scale CO_2 fluxes, Atmos. Chem. Phys., 7, 3737–3747, doi:10.5194/acp-7-3737-2007, 2007.

Jacob, D. J., Prather, M. J., Rasch, P. J., Shia, R.-L., Balkanski, Y. J., Beagley, S. R., Bergmann, D. J., Blackshear, W. T., Brown, M., Chiba, M., Chipperfield, M. P., de Grandpré, J., Dignon, J. E., Feichter, J., Genthon, Ch., Grose, W. L., Kasibhatla, P. S., Köhler, I., Kritz, M. A., Law, K., Penner, J. E., Ramonet, M., Reeves, C. E., Rotman, D. A., Stockwell, D. Z., van Velthoven, P. F. J., Verver, G., Wild, O., Yang, H., and Zimmermann, P.: Evaluation and intercomparison of global atmospheric transport models using ^{222}Rn and other short-lived tracers, J. Geophys. Res., 102, 5953–5970, 1997.

Kuiken, T., Zhang, H., Gustin, M., and Lindberg, S.: Mercury emission from terrestrial background surfaces in the eastern USA, Part 1: Air/surface exchange of mercury within a southeastern deciduous forest (Tennessee) over one year, Appl. Geochem., 23, 345–355, 2008a.

Kuiken, T., Gustin, M., Zhang, H., Lindberg, S., and Sedinger, B.: Mercury emission from terrestrial background surfaces in the eastern USA, Part 2: Air/surface exchange of mercury within forests from South Carolina to New England, Appl. Geochem., 23, 356–368, 2008b.

Lin, C.-J., Pongprueksa, P., Lindberg, S. E., Pehkonen, S. O., Byun, D., and Jang, C.: Scientific uncertainties in atmospheric mercury models 1: model science evaluation, Atmos. Environ., 40, 2911–2928, 2006.

Lindberg, S. E., Hanson, P. J., Meyers, T. P., and Kim, K.-H.: Air/surface exchange of mercury vapor over forests – the need for a reassessment of continental biogenic emissions, Atmos. Environ., 32, 895–908, 1998.

Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, E., and Seigneur, C.: A synthesis of progress and uncertainties in attributing the sources of mercury in deposition, Ambio, 36, 19–32, 2007.

Mason, R. P.: Mercury emissions from natural processes and their importance in the global mercury cycle, in: Mercury Fate and Transport in the Global Atmosphere,edited by: Pirrone, N. and Mason, R., Springer Verlag, Dordrecht, 173–191, 2009.

Mergler, D., Anderson, H. A., Chan, L. H. M., Mahaffey, K. R., Murray, M., Sakamoto, M., and Stern, A. H.: Methyl mercury exposure and health effects in humans: a worldwide concern, Ambio, 36, 3–11, 2007.

Munthe, J., Wängberg, I., Pirrone, N., Iverfeldt, A., Ferrara, R., Ebinghaus, R., Feng, X., Gardfeldt, K., Keeler, G., Lanzillotta, E., Lindberg, S. E., Lu, J., Mamane, Y., Prestbo, E., Schmolke, S., Schroeder, W. H., Sommar, J., Sprovieri, F., Stevens, R. K., Stratton, W., Tun-

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13, 8213–8231, 2013

cel, G., and Urba, A.: Intercomparison of methods for sampling and analysis of atmospheric mercury species, Atmos. Environ., 35, 3007–3017, 2001.
Obrist, D., Conen, F., Vogt, R., Siegwolf, R., and Alewell, C.: Estimation of Hg^0 exchange between ecosystems and the atmosphere using ^{222}Rn and Hg^0 concentration changes in the stable nocturnal boundary layer, Atmos. Environ., 40, 856–866, 2006.
Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R. B., Friedli, H. R., Leaner, J., Mason, R., Mukherjee, A. B., Stracher, G. B., Streets, D. G., and Telmer, K.: Global mercury emissions to the atmosphere from anthropogenic and natural sources, Atmos. Chem. Phys., 10, 5951–5964, doi:10.5194/acp-10-5951-2010, 2010.
Scheel, H. E., Brunke, E.-G., and Seiler, W.: Trace gas measurements at the monitoring station Cape Point, South Africa, between 1978 and 1988, J. Atmos. Chem., 11, 197–210, 1990.
Scheuhammer, A. M., Meyer, M. W., Sandheinrich, M. B., and Murray, M. W.: Effects of environmental methylmercury on the health of wild bird, mammals, and fish, Ambio, 36, 12–18, 2007.
Selin, N. E., Jacob, D. J., Yantosca, R. M., Strode, S., Jaeglé, L., and Sunderland, E. M.: Global 3-D land-ocean-atmosphere model for mercury: present-day versus preindustrial cycles and anthropogenic enrichment factors for deposition, Global Biogeochem. Cy., 22, GB2011, doi:10.1029/2007GB003040, 2008.
Slemr, F., Schuster, G., and Seiler, W.: Distribution, speciation, and budget of atmospheric mercury, J. Atmos. Chem., 3, 407–434, 1985.
Slemr, F., Brunke, E.-G., Labuschagne, C., and Ebinghaus, R.: Total gaseous mercury concentrations at the Cape Point GAW station and their seasonality, Geophys. Res. Lett., 35, L11807, doi:10.1029/2008GL033741, 2008.
Smith-Downey, N. V., Sunderland, E. M., and Jacob, D. J.: Anthropogenic impacts on global storage and emissions of mercury from terrestrial soils: insights from a new global model, J. Geophys. Res., 115, G03008, doi:10.1029/2009JG001124, 2010.
Soerensen, A. L., Skov, H., Jacob, D. J., Soerensen, B. T., and Johnson, M. S.: Global concentrations of gaseous elemental mercury and reactive gaseous mercury in the marine boundary layer, Environ. Sci. Technol., 44, 7425–7430, 2010.
Song, X. and Van Heyst, B.: Volatilization of mercury from soils in response to simulated precipitation, Atmos. Environ., 39, 7494–7505, 2005.
Whittlestone, S. and Zahorowski, W.: Baseline radon detectors for shipboard use: development and deployment in ACE-1, J. Geoph. Res., 103, 16743–16751, 1998.

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13, 8213–8231, 2013

Wilson, S. R., Dick, A. L., Fraser, P. J., and Whittlestone, S.: Nitrous oxide flux estimates for south-eastern Australia, J. Atmos. Chem., 26, 169–188, 1997.

Xin, M., Gustin, M., and Johnson, D.: Laboratory investigation of the potential for re-emission of atmospherically derived Hg from soils, Environ. Sci. Technol., 41, 4946–4951, 2007.

Zahorowski, W., Chambers, S. D., and Henderson-Sellers, A.: Ground based radon-222 observations and their application to atmospheric studies, J. Environ. Radioactiv., 76, 3–33, 2004.

Zhang, H. and Lindberg, S. E.: Processes influencing the emission of mercury from soils: a conceptual model, J. Geophys. Res., 104, 21889–21896, 1999.

Zhang, K., Feichter, J., Kazil, J., Wan, H., Zhuo, W., Griffiths, A. D., Sartorius, H., Zahorowski, W., Ramonet, M., Schmidt, M., Yver, C., Neubert, R. E. M., and Brunke, E.-G.: Radon activity in the lower troposphere and its impact on ionization rate: a global estimate using different radon emissions, Atmos. Chem. Phys., 11, 7817–7838, doi:10.5194/acp-11-7817-2011, 2011.

Zhang, L., Paige Wright, L., and Blanchard, P.: A review of current knowledge concerning dry deposition of atmospheric mercury, Atmos. Environ., 43, 5853–5864, 2009.

ACPD
13, 8213–8231, 2013

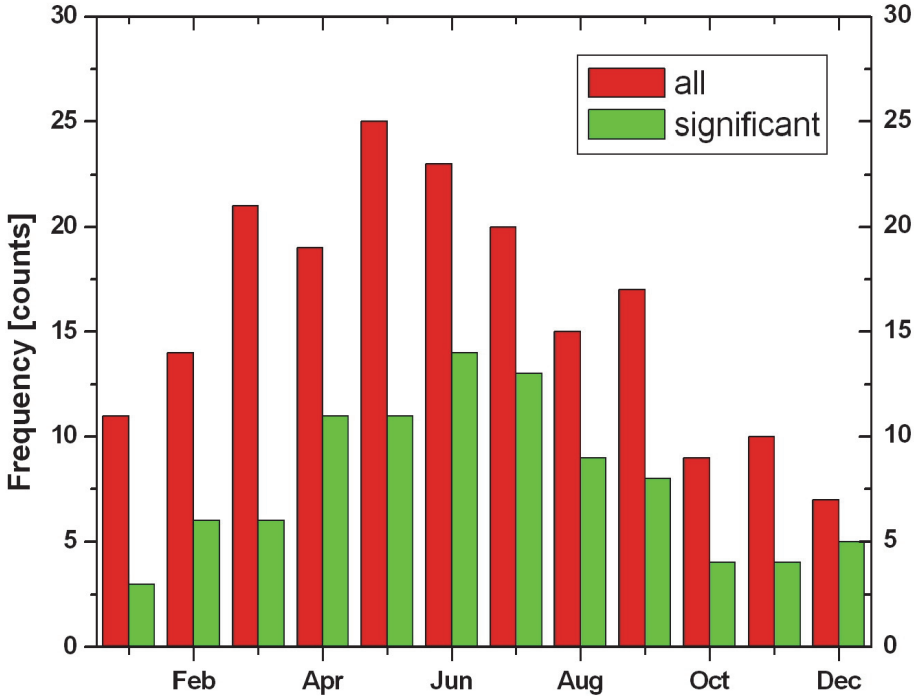

Fig. 1. Seasonal frequency of all ^{222}Rn events and those with significant GEM vs. ^{222}Rn correlations.

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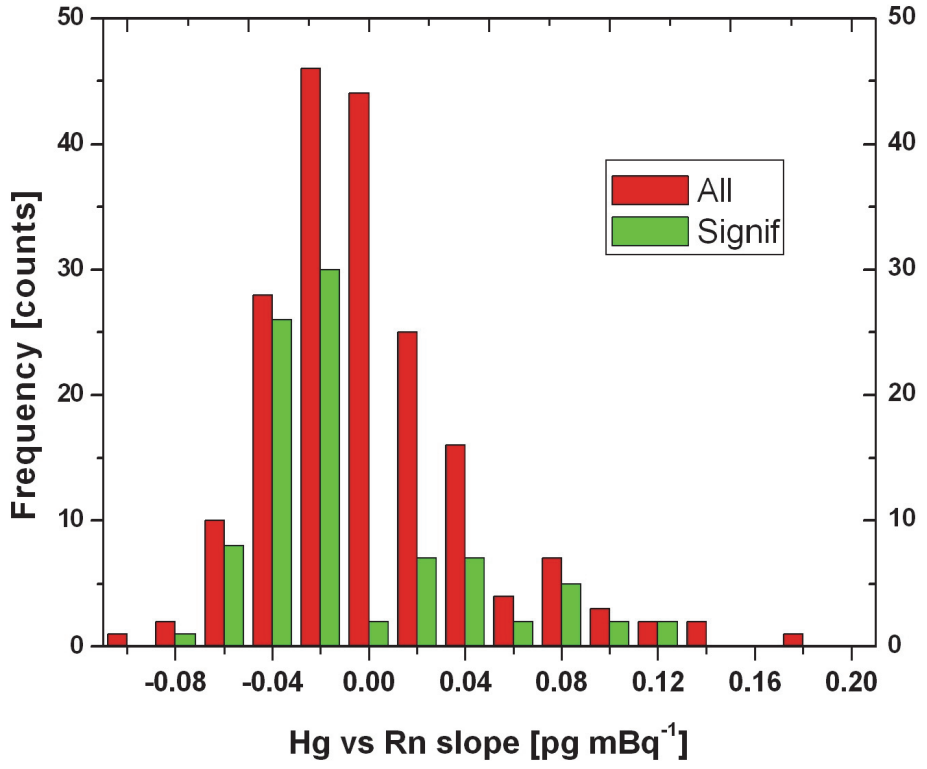

Fig. 2. Frequency distribution of all Hg/^{222}Rn slopes and only of those which are significant.

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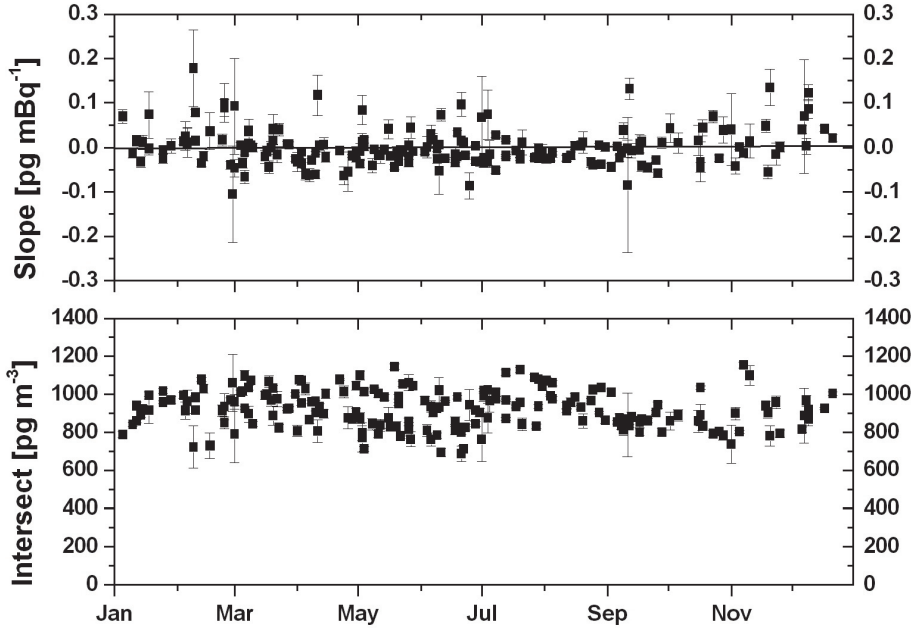

Fig. 3. Seasonal variation of the GEM/222Rn slopes (upper figure) and the GEM intercepts (lower figure).

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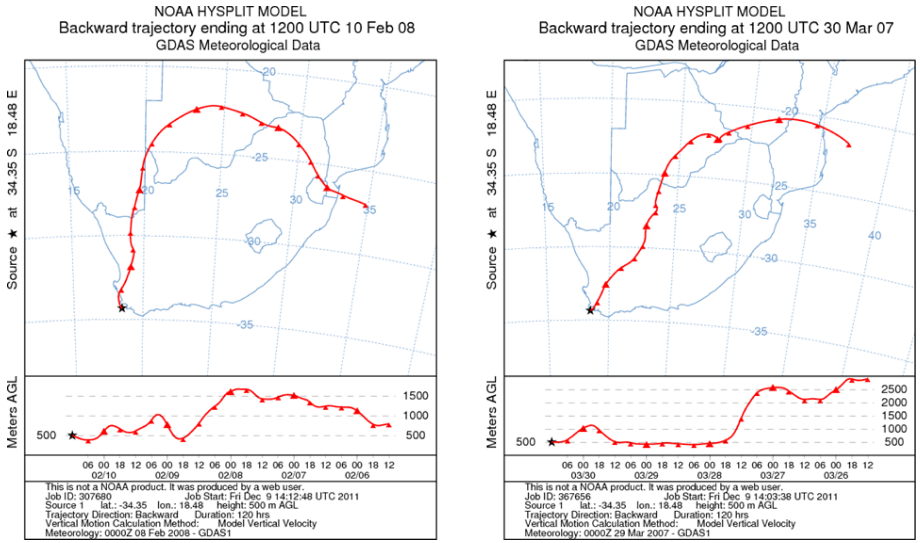

Fig. 4. Backward trajectory for 12:00 of 10 February 2008 (left panel), and 12:00 of 30 March 2007 (right panel). The GEM/^{222}Rn flux ratio was $+0.077 \pm 0.008\,\mathrm{pg\,mBq^{-1}}$ for the event on 10 February 2008, and $-0.026 \pm 0.005\,\mathrm{pg\,mBq^{-1}}$ for the event on 30 March 2007.

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